



## Short communication

Effect of electrochemical treatment in  $\text{H}_2\text{SO}_4$  aqueous solution on carbon material derived from cellulose with added guanidine phosphate

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## H I G H L I G H T S

- Combination of the addition of guanidine phosphate with electrochemical treatment was proposed.
- The capacitance value in 1 M  $\text{H}_2\text{SO}_4$  was greater than  $350 \text{ F g}^{-1}$  at  $50 \text{ mA g}^{-1}$  after the process.
- The capacitance values at less than  $50 \text{ mA g}^{-1}$  were more than  $300 \text{ F g}^{-1}$ .
- The increment should be related to the reaction of the electrolysis of water.
- The XPS data indicated the increase in both the O atoms and the N atoms after the electrochemical treatment.

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## A B S T R A C T

The electrochemical treatment in a 1 M  $\text{H}_2\text{SO}_4$  aqueous solution is applied to the carbon material synthesized from cellulose mixed with guanidine phosphate. The capacitance value increased by the addition of guanidine phosphate; furthermore, the value significantly increased by the electrochemical treatment and was higher than  $350 \text{ F g}^{-1}$  at  $50 \text{ mA g}^{-1}$ . The process used in this study, that is, removing the lignin from wood waste products, such as bamboo, and then mixing with guanidine phosphate before the heat treatment followed by an electrochemical treatment, should be of benefit for the synthesis of a high performance material for the electrodes of electrochemical capacitors. The significant enhancement of the capacitance value appears in the range of 1.5 V ~ 2.8 V vs. Ag/AgCl for the applied maximum voltage. This voltage range is consistent with the voltage for the significant enhancement of the current value in the CV curve. The change in the capacitance value should be related to the electrochemical reaction of the water electrolysis. The XPS data indicated that the concentrations of both the N atom and the O atom on the surface increased after the electrochemical process.

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## 1. Introduction

Recently, many research studies have been performed for the development of electrochemical capacitors such as the electrical double layer capacitor (EDLC). Many of the reports on the electrochemical capacitor are related to improvement of the electrode material because the electrode is the most important part for the storage. Some papers have reported that the addition of a hetero element such as N, P, etc., is effective for improving the capacitance [1–3], and the effect of the addition has been under discussion [4].

We have already reported that the addition of guanidine phosphate is an effective way to improve the capacitive performance of

the carbon material derived from starch [5]. This method, that is, the addition of guanidine phosphate before the heating process, is simple, easy, safe, and inexpensive. Therefore, this method should be valuable in practical use. The chemical structure of cellulose is similar to that of starch because both of them are polysaccharides. Cellulose is a constituent of plants. If the method proposed in this study was effective for improving the capacitance performance, then we can produce a high performance material at a low price. Therefore, we can expect that guanidine phosphate can improve the capacitance value of the carbon material derived from cellulose. Increasing the surface area is one of the most popular approaches for changing the capacitance value of an electrical double layer capacitor. However, some reports indicated that after the activation process for increasing the surface area, that is, a heating process, the capacitance value was not improved, although the surface area was increased. The decrease in the ratio of the N atoms in the

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material, which should be caused by the heating process, could be the reason for the suppression of the capacitive performance in spite of the higher surface area. It is known that electrochemical activation is one of the methods for enhancing the capacitance value [6]. An aqueous or non-aqueous solution was used as the solution for the electrochemical treatment. For the aqueous solution, certain types of carbon materials were used for the treatment. Momma et al. reported that electrochemical oxidation enhanced the capacitance value of active carbon fibers although the electrode inner resistance increased [7]. They considered that the reason for the enhancement of the capacitance value was cleaning of the surface, refining the terminal functional group at the surface, changing the pore size, etc. Milczarek et al. performed the electrochemical activation of commercial activated carbon fibers in deionized water by applying a constant voltage of 50 V [8]. They concluded that the high specific surface area, high oxygen content, and good wettability were the reasons for the improvement. Dekanshi et al. used glassy carbon electrodes for the treatment in a 0.5 M H<sub>2</sub>SO<sub>4</sub> or 1 M NaOH aqueous solution [9]. They found that the amount of the charge stored in the electrode repeatedly increased and decreased when the time of the polarization process increased. The reason for the repetition was explained by the repetition of the process which involved the surface layer oxidation, graphite oxide layer growth, and mechanical destruction of the surface. Shi et al. investigated the effect of the electrochemical treatment in a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution on the surface morphology of glassy carbon [10]. Their results also showed that the treatment changed the surface structure of the electrode.

It should be presumed that electrochemical treatment is an effective way to improve the capacitance value of the carbon material containing added guanidine phosphate, because some papers reported that the treatment enhanced the capacitance value of the carbon material which did not contain N atoms. Moreover, there is no heat treatment process, which could decrease the percentage of N atoms in the material, during the activation method. Therefore, in this study, we attempted to apply the combination of the addition of guanidine phosphate with electrochemical activation to cellulose or bamboo having the lignin removed as the cellulose source.

## 2. Experimental

Cellulose (Cellulose, microcrystalline; Alfa Aesar) was mixed with guanidine phosphate at the ratio weight of 20:1 or 5:1, and the mixed powder was then added to distilled water. The slurry was dried in a dryer at 80 °C until the slurry became completely dry (approximately 72 h). The dried powder was heated at 800 °C for 1 h under flowing N<sub>2</sub> (50 mL min<sup>-1</sup>). These powders were used the BET method and CHN-corder measurements. The powder prepared by the heat treatment, acetylene black, and Teflon powder were mixed at an 8:1:1 ratio to form a sheet. The sheet was cut and was then used as the electrode for the electrochemical measurements. The sheet was placed in a three-electrode cell, and Pt plates were used as the counter electrode and the collector electrode and a Ag/AgCl electrode was used as the reference electrode. The electrochemical activation was performed in the cell. The

electrochemical activation process used in this study is as follows. Voltammetric cycles were performed from -0.2 V to 3.0 V vs. Ag/AgCl at the scan rate of 100 mV s<sup>-1</sup> on the sample in the three-electrode cell. Ten cycles were defined as 1 set. The capacitance value at 50 mA g<sup>-1</sup> was measured after each set. The capacitance values were calculated from the data for the charging process. Raman measurements (NRS-5100, JASCO) were performed on the sheet samples using a 532 nm laser in order to investigate the condition of the samples. The XPS measurements (AXIS-NOVA, Shimadzu) were performed on the sheet samples using Al K $\alpha$  X-rays.

## 3. Results and discussion

### 3.1. Sample condition after heat treatment

The results of the CHN-corder, and BET surface area measurements, and yield (100\*(the weight after the heat treatment)/(before the heat treatment)) are summarized in Table 1. The samples with the added guanidine phosphate contained N atoms, and the percentages of the N atoms increased with the increasing ratio of the added guanidine phosphate. However, the amounts of the N atoms were less than 4 wt.% at most. When guanidine phosphate was added, the percentage of the N atoms in the sample derived from bamboo was almost the same as that of the sample derived from cellulose. The BET surface area of the sample synthesized from only cellulose was greater than 1200 m<sup>2</sup> g<sup>-1</sup>. For the samples with added guanidine phosphate, the surface areas were about half that of the sample with only cellulose. One of the reasons for the decrease in surface area might be the residue derived from the guanidine phosphate, which should have a small surface area. The surface area of the sample derived from bamboo was higher than that of the cellulose with added the guanidine phosphate. The reason for this difference may be the microstructure of bamboo, which is the starting material. The yield improved by the addition of guanidine phosphate regardless of the cellulose source. The flame-retardant effect of guanidine phosphate on the cellulose could be the reason for the enhanced yield.

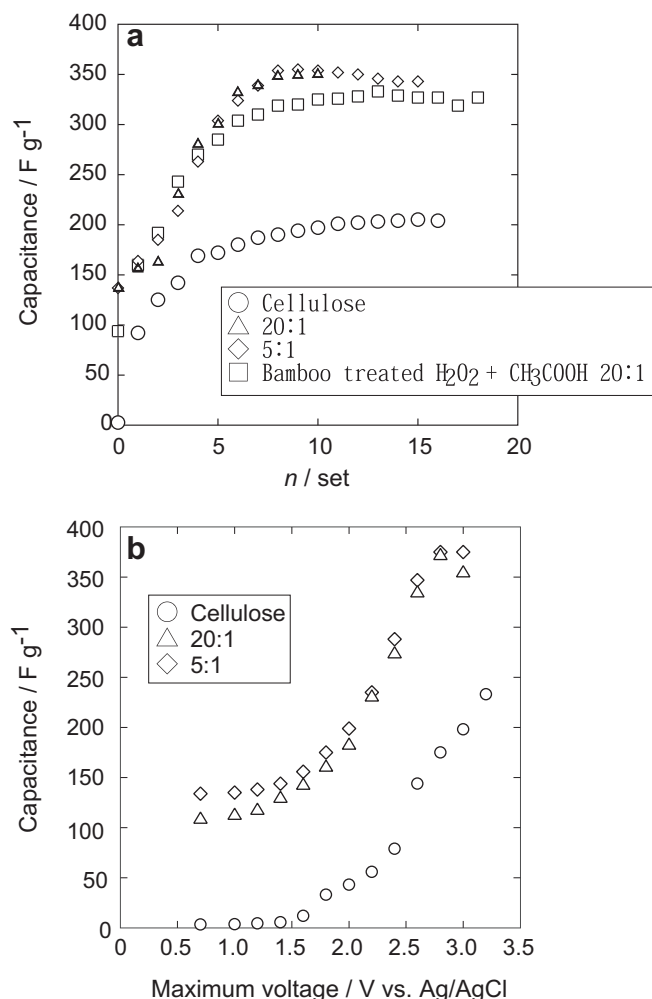
### 3.2. Effect of electrochemical treatment

Numerous sets for the electrochemical activation dependence on capacitance values are shown in Fig. 1(a). The capacitance value increased with the increasing number of sets for all the samples up to ca. 10 times. In the case of only cellulose, the capacitance value before the electrochemical activation was a very low value, and that the value after the electrochemical activation (9 times) was ca. 200 F g<sup>-1</sup>. It should be noted from this result that the process applied in this study is effective on the carbon material derived from cellulose for enhancing the capacitance value. The capacitance values before the electrochemical activation process for the samples with the added guanidine phosphate were ca. 140 F g<sup>-1</sup>. We have already reported that the addition of guanidine phosphate to starch before the heat treatment for the preparation of a carbon material is effective for enhancing of the capacitance value [5]. The chemical structure of cellulose is similar to that of starch because

**Table 1**  
Experimental results of CHN corder, BET surface area, and yield after heat treatment.

	H/wt. %	C/wt. %	N/wt. %	Others/wt. %	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>	Yield/%
Cellulose	1.32	82.92	—	15.76	1284	14
Cellulose: guanidine phosphate = 5: 1	2.29	72.24	3.81	21.66	739	22
Cellulose: guanidine phosphate = 20: 1	1.70	82.49	2.34	13.47	678	21
Bamboo after delignification: guanidine phosphate = 20:1	1.83	71.47	2.36	24.34	1294	24





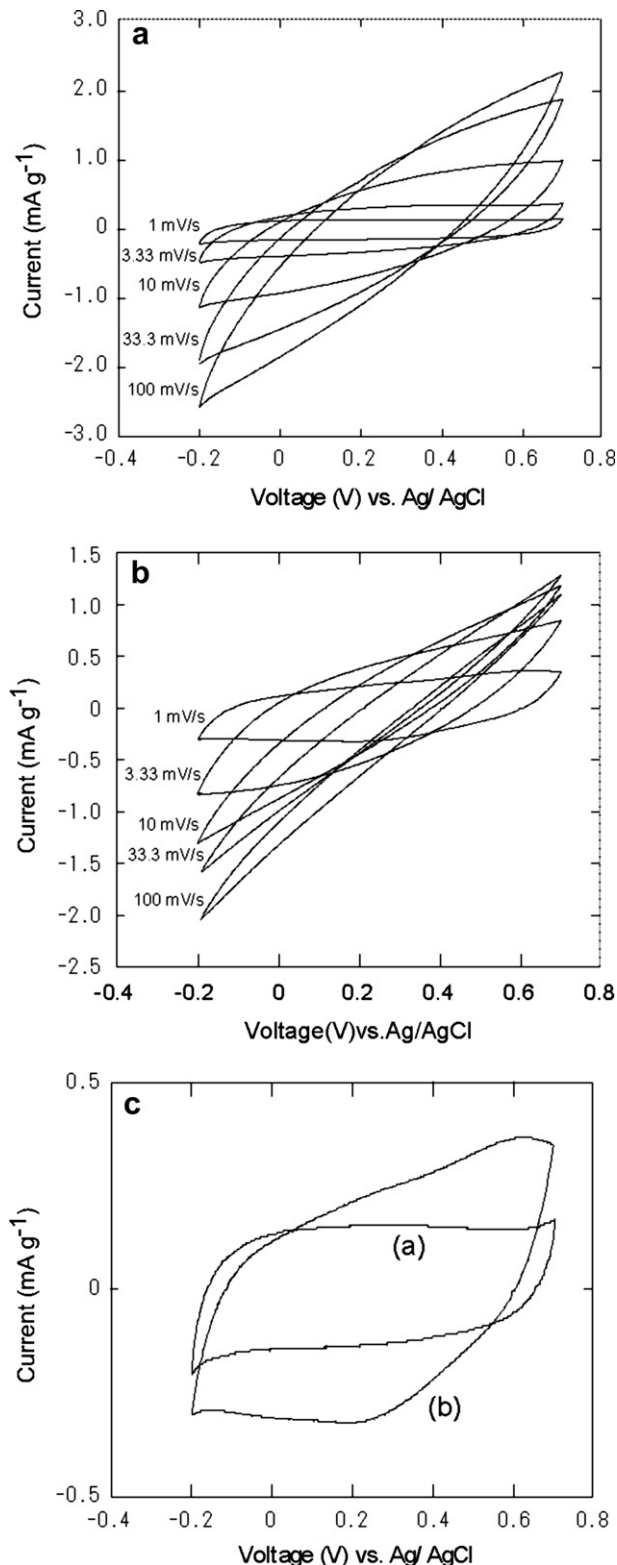
**Fig. 1.** Effects of electrochemical treatment. (a), The numerous sets for electrochemical activation dependence on capacitance values. (1 set is 10 cycles at  $-0.2\ V \sim 3.0\ V$  Ag/AgCl.) (b), Maximum voltage applied to the sample dependence of the capacitance values.

glucose is a constituent of both cellulose and starch. Therefore, the change in the capacitance value for cellulose should be reasonable due to the addition of guanidine phosphate. The capacitances value significantly increased with the increasing number of electrochemical activation processes and was greater than  $350\ F\ g^{-1}$ .

We thought that lignin, which is one of the primary constituents in plants, might prevent the improvement in capacitance. Therefore, a treatment with  $H_2O_2$ – $CH_3COOH$  was performed for the removing lignin from the bamboo. The capacitance value after the electrochemical activation (13 times) was  $333\ F\ g^{-1}$ . These capacitance values were high and similar to that for the cellulose mixed with guanidine phosphate. Therefore, the method used in this study should be of benefit for the utilization of bamboo.

Raman measurements were performed in order to investigate the reason for the improved capacitance value. The Raman spectra of the samples are shown in Fig. S1. The spectrum of the sample after the electrical treatment was almost the same as that of the sample before the electrical activation. Therefore, the bulk structure of the sample should be unchanged after the activation.

The CV curves of the samples before the electrochemical activation are shown in Fig. 2. Moreover, the area of the CV curves for the high scan rate decreased after the electrochemical activation, which should mean that the capacitance value for the high scan



**Fig. 2.** CV curves of the samples (cellulose: guanidine phosphate = 5:1) (a), before electric field activation; (b), after electric field activation (15 sets); (c), magnified CV curves at the scan rate of  $1\ mV\ s^{-1}$ .

rate decreased after the electrochemical activation. However, the magnified CV curve for the scan rate of  $1\ mV\ s^{-1}$  indicated that the area of the CV curve increased after the electrochemical activation (Fig. 2(c)). Moreover, the shape of the curve changed after the



activation. Some papers have reported that peaks assigned to a redox reaction in the CV curves appeared or increased after an electrochemical oxidation process in a  $\text{H}_2\text{SO}_4$  solution [7–9]. The electrical potential of the peaks related to a redox reaction reported in refs. 7 and 9 are similar to that of the change in the intensity in the CV curve of (b) in Fig. 2(c), that is, at ca. 0.2 V and ca. 0.5 V vs. Ag/AgCl. It is presumed that the carbon surface was anodically oxidized during the electrochemical activation. Hsieh and Teng [11] proposed that the oxygen functional group containing the C=O bond, such as a carbonyl group and quinone group, was in the following equilibrium state:



where  $>\text{C}_x\text{O}/\text{H}^+$  is a proton adsorbed by the oxygen functional group. At the negative electrical potential, the surface condition was proposed as follows:



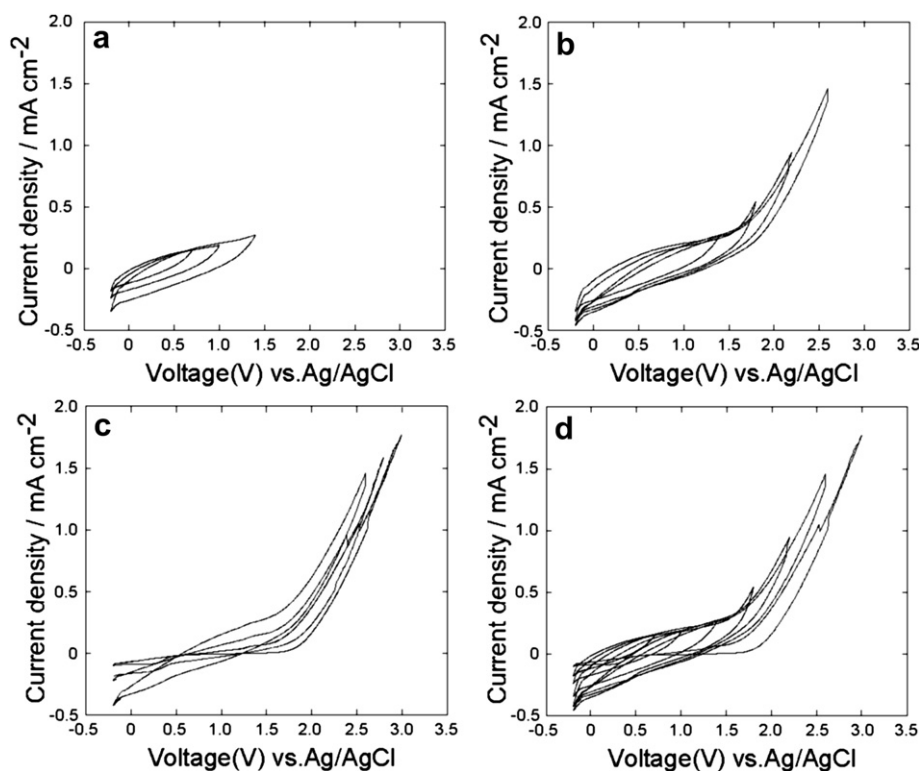
where  $>\text{C}_x\text{OH}$  is a hydroquinone-type complex and  $\text{e}^-$  is an electron. These equilibrium reactions could be the origin of the change in the intensity in the CV curve of (b) in Fig. 2(c). The decreases in the area of the CV curve at a high scan may be reasonable because the reaction rates of eqs. (1) and (2) should be slow. The oxygen functional group containing the C=O bond should be introduced only on the surface because the Raman spectrum was unchanged after the activation.

In order to analyze the effect of the electrochemical activation treatment applied in this study, the voltage dependence on the capacitance value was investigated in detail. The CV process was performed 10 times from  $-0.2$  V to  $0.6$  V, and then the capacitance value was measured at the condition of  $50 \text{ mA g}^{-1}$ . Next, the sample

was subjected to the CV process 10 times from  $-0.2$  V to  $1.0$  V, and then the capacitance value was measured. In this way, the applied voltage increased in increments of  $0.2$  V. The CV curves for the sample (cellulose: guanidine phosphate = 5:1) are shown in Fig. 3. The capacitance value dependence on the applied maximum voltage is shown in Fig. 1(b). As shown in Fig. 3, the current density in the oxidative process was almost the same until the oxidation potential was ca.  $1.5$  V. The current density significantly increased with the increasing applied maximum voltage in the range of  $1.5$  V– $2.8$  V. The reason for the high current value should be the electrolysis of water, which is the solvent in the cell. On the other hand, as shown in Fig. 1(b), the capacitance value increased from ca.  $1.5$  V and then rapidly increased from ca.  $2.0$  V to ca.  $2.8$  V. It should be noted that the tendency of the voltage dependence of the capacitance value was similar to that of the current density. When the applied maximum voltage was  $2.8$  V– $3.0$  V, the value of current density at  $-0.2$  V decreased with the increasing applied maximum voltage, although that value increased with the increasing applied maximum voltage up to  $2.6$  V. The capacitance value was almost independent of the voltage in the range of  $2.8$  V– $3.0$  V.

When a cell without the sample was also used for the experiment, the current value was almost the same as that of the cell containing the sample. This result should indicate that the electrochemical reaction at a high voltage occurred not on the surface of the sample, but on the Pt plate. An electrochemical reaction, such as the electrolysis of water, may be related to the significant enhancement of the capacitance value. Moreover, the decrease in the reduction current with the increasing applied maximum voltage at  $2.8$  V– $3.0$  V (Fig. 3(c)) may be related to the suppression of the increment in the capacitance value at  $2.8$  V– $3.0$  V.

The current density dependence of the capacitance values of the sample (cellulose: guanidine phosphate = 20:1) after the electrochemical treatment of Fig. 1(a) is shown in Fig. 4. The capacitance



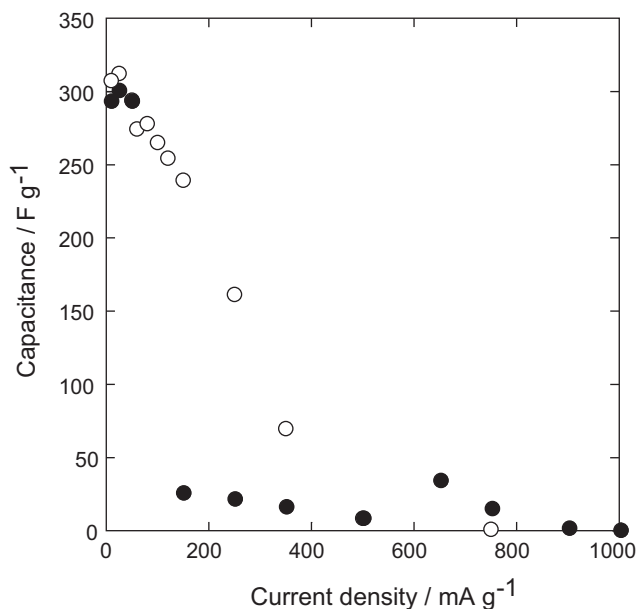
**Fig. 3.** CV curves of the sample (cellulose: guanidine phosphate = 5:1). (a), from  $-0.2$  V– $0.7$  V to  $-0.2$  V– $1.4$  V; (b), from  $-0.2$  V– $1.4$  V to  $-0.2$  V– $2.6$  V; (c), from  $-0.2$  V– $2.6$  V to  $-0.2$  V– $3.0$  V; (d), from  $-0.2$  V– $0.7$  V to  $-0.2$  V– $3.0$  V.



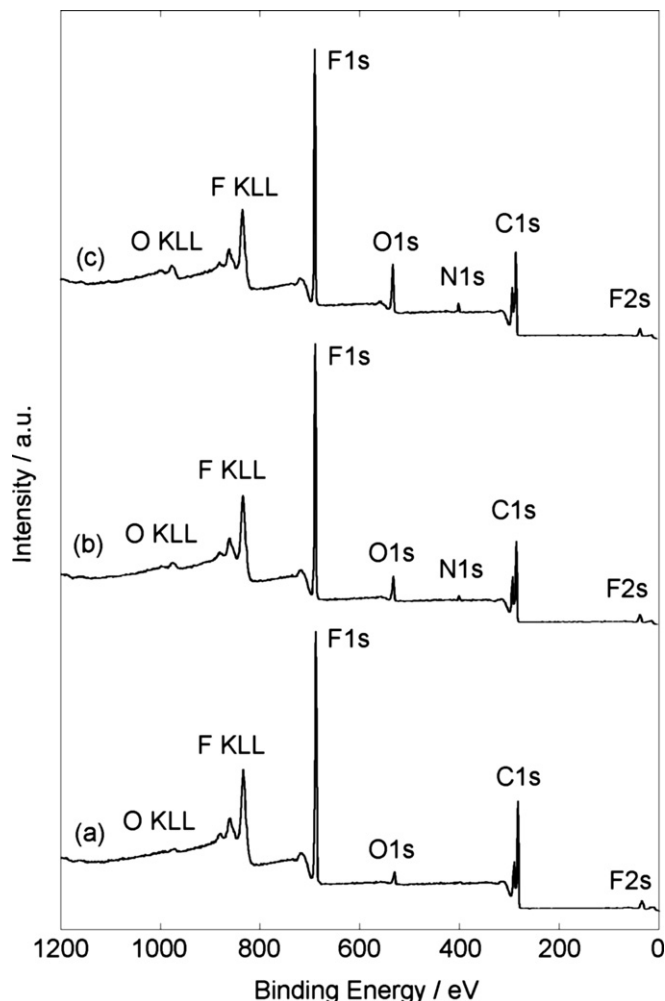
value significantly decreased with the increasing current density during the charging process. The small areas of the CV graphs at the high scan rate in Fig. 2 were consistent with the small capacitance values at the high current densities. The reason for the dependence of the current density on the capacitance value could be explained by the existence of the functional groups expressed by eqs. (1) and (2). Because the reaction rate of eqs. (1) and (2) should be slow, the capacitance value drastically decreased at the high current density. The experimental results should mean that the material could be used only at low current density. Moreover, it should be noted that the capacitance value depended on the direction of the measurement, that is, the capacitance values measured from a low current density to a high current density were higher than those measured from a high current density to a low current density. These results could indicate that the high current density was harmful to the material. However, when the current density was lower than  $50 \text{ mA g}^{-1}$ , the capacitance values were *ca.*  $300 \text{ F g}^{-1}$  regardless of the direction of the measurement.

The XPS spectra for a wide scan of the cellulose mixed with guanidine phosphate sample are shown in Fig. 5. The peak assigned to oxygen was enhanced after the electrochemical measurement (CV measurement and charge–discharge measurement) for one time. Moreover, the peak intensity further increased by the electrochemical activation. This result should agree with the above discussion. Interestingly, the peak assigned to the N atom appeared after the electrochemical measurement, and the peak intensity increased by the electrochemical activation. As for the sample before the electrochemical measurement, we could not find the peak assigned to the N atom in spite of the fact that the sample before the electrochemical measurement should contain nitrogen as shown in Table 1. The amount of the N atoms on the surface should increase during the electrochemical measurement and the electrochemical activation.

The atomic concentrations on the surface calculated from the XPS data of wide scans are shown in Table 2. The concentrations of the O atom increased after the electrochemical process such as the measurement and the treatment. Moreover, the concentrations of



**Fig. 4.** Current density dependence of capacitance values of the sample (cellulose: guanidine phosphate = 20:1) after the electrochemical treatment in Fig. 1(a). ○: measured from low current density to high current density, ●: measured from high current density to low current density. (The capacitance values were calculated from the charging process data.)



**Fig. 5.** XPS spectra for wide scans of the samples. (a), Before the electrochemical measurement; (b), after the measurement for 1 time and before the electrochemical activation; (c), after the electrochemical activation.

the N atom also increased after these electrochemical processes. The change in the concentration of the O atom should be related to the enhancement of the capacitance value. The change in the concentration of the N atom is also related to the enhancement of the capacitance value. However, it should be presumed that the main reason for the enhancement of the capacitance value was the increase in the concentration of the O atoms on the surface because the absolute value of the N atom concentration was low. The reason for the change in the concentration of oxygen should be the electrochemical oxidation in the high potential range during the electrochemical processes. The possible reason for the change in the concentration of nitrogen was the introduction of the N atoms onto the surface or the preferential removal of the C atoms on the surface. For the introduction of the N atoms, the possible origin of

**Table 2**

The atomic concentrations on the surface calculated from the XPS data of wide scans.

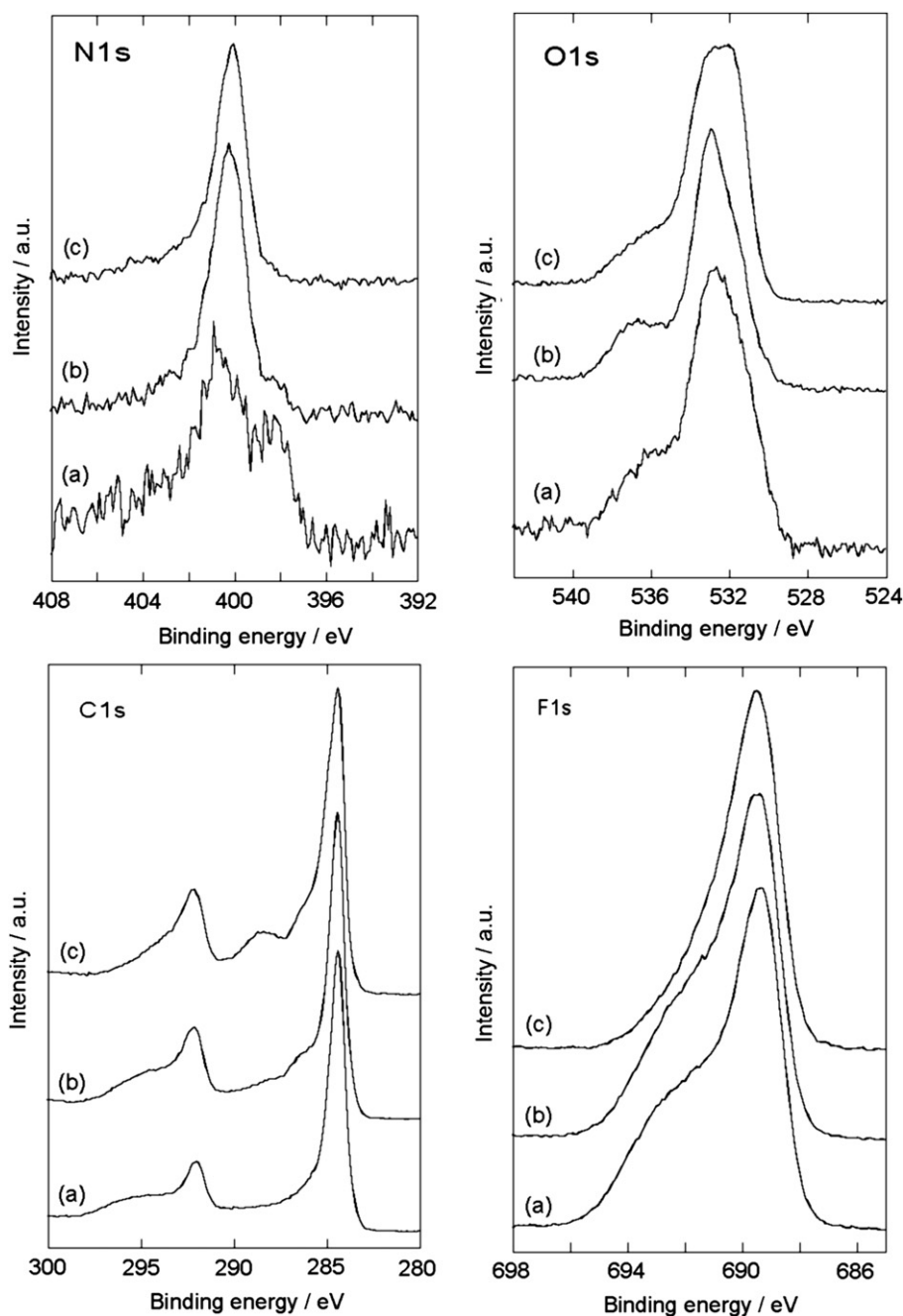
	C/%	N/%	O/%	F/%
Before the electrochemical measurement	59.39	0.05	2.77	37.79
After the measurement for 1 time and before the electrochemical treatment	54.55	1.28	5.47	38.70
After the electrochemical treatment	55.52	1.94	9.36	33.18



the nitrogen may be the  $N_2$  bubbling of the 1 M  $H_2SO_4$  solution as the pretreatment before the electrochemical measurement or the dissolved  $N_2$  from the air during the electrochemical processes. However, it should be unlikely to produce the reaction due to the introduction of the N atoms because  $N_2$  should be stable in the potential range. The preferential removal of the C atoms may occur in the high voltage region of the electrochemical processes.

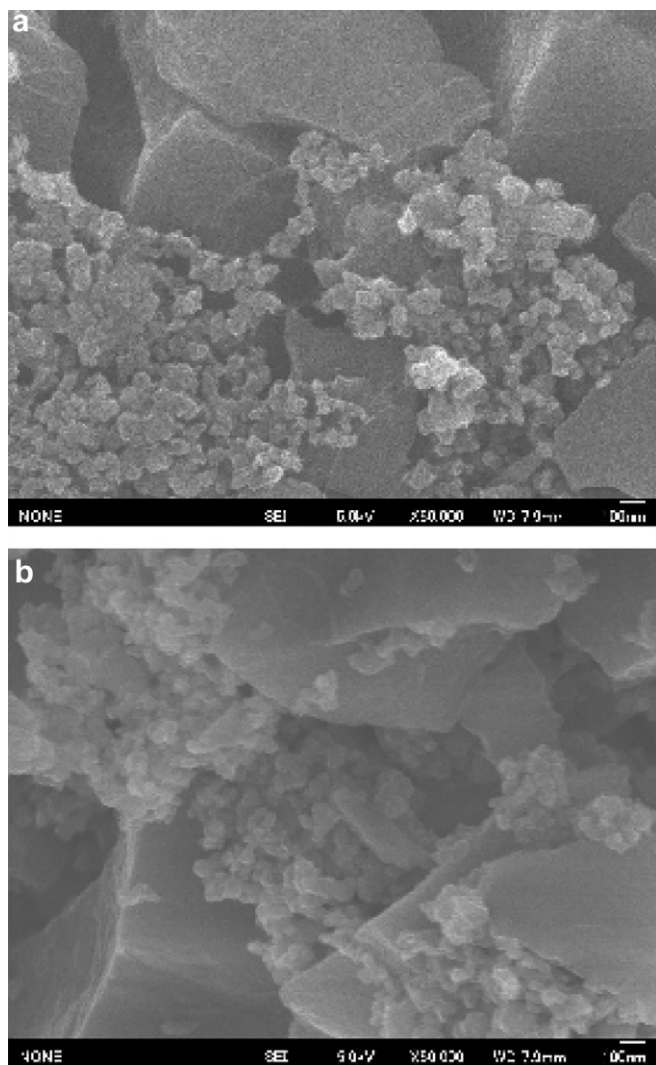
The XPS spectra for the narrow scan of the samples of the cellulose mixed with guanidine phosphate are shown in Fig. 6. We could detect a small peak assigned to nitrogen in the spectrum for the sample before the electrochemical measurement. The peak intensity at *ca.* 400 eV significantly increased during the electrochemical measurement and the electrochemical activation. The

peak positions of the samples could not be rigorously discussed because these data could not be calibrated. However, it should be noted that the N atom species is of one type because of only one peak. As for the peak assigned to the O atom, the peak at *ca.* 532 eV increased with the electrochemical processes. As for the peak assigned to the C atom, a new peak appeared at *ca.* 288 eV after the electrochemical activation. Although the peak positions of the samples could not be rigorously discussed, these results should mean that the oxygen, which combined with the carbon, was introduced onto the surface. The presumed condition from the relative peak positions could be the  $-NH-C=O$  group or the  $-O-C=O$  group. As for the peak assigned to the F atom, the peak at *ca.* 693 eV gradually decreased after the electrochemical measurement



**Fig. 6.** XPS spectra narrow scans of the samples. (a), Before the electrochemical measurement; (b), after the measurement for 1 time and before the electrochemical activation; (c), after the electrochemical activation.





**Fig. 7.** SEM images of the sample before and after the electrochemical treatment in Fig. 1(a). (a), Before the electrochemical measurement; (b), after the electrochemical activation.

and the electrochemical activation. The O atoms might be introduced at the position of the F atom derived from the peak at ca. 693 eV.

SEM images are shown in Fig. 7. As shown in Fig. 7, the microstructure of the sample was independent of the electrochemical treatment applied in this study. Some papers reported that the microstructure of the carbon material of the electrode changed after the electrochemical treatment [6–10]. When glassy carbon was used as the electrode, a surface layer oxidation and graphite oxide layer growth occurred on the electrode, resulting in a surface

structure change [9,10]. The samples of these studies were also electrochemically oxidized by the electrochemical activation process. However, for this study, the sample should not be directly oxidized during the process. The sample in this study stayed on the Pt electrode which electrochemically oxidized water and produced  $O_2$ . This difference should be the reason for the unchanged pore structure.

#### 4. Conclusions

The combination of the addition of guanidine phosphate and electrochemical activation was performed for enhancing the capacitance value of the carbon material derived from cellulose. This treatment drastically improved the capacitance value. The treatment was applied to bamboo after a delignification process. The capacitance value was significantly increased by the treatment. The treatment used in this study should be effective for the beneficial use of waste wood products such as bamboo. The improvement in the capacitance value appeared at an applied maximum voltage of 1.5 V–2.8 V vs. Ag/AgCl. This was about the same range as the voltage for the electrolysis of water in the cell. The capacitance value of the sample after the treatment was greater than  $350 \text{ F g}^{-1}$  at  $50 \text{ mA g}^{-1}$ . Although the capacitance value rapidly decreased with the increasing current density, the capacitance value was greater than  $300 \text{ F g}^{-1}$  when the current density was less than  $50 \text{ mA g}^{-1}$ . The increase in the concentrations of both the N atoms and the O atoms on the surface, especially the change in the O atom, should be the reason for the enhanced capacitance value after the electrochemical process.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2012.10.049>.

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